

THE PROS AND CONS OF POSSIBLE ELECTRON TRANSFER STEPS IN AROMATIC NITRATION REACTIONS

FINN RADNER

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Organization LUND UNIVERSITY Chemical Center	Document name DOCTORAL DISSERTATION	
	Date of issue October 1985	
	CODEN: LUNK DL/(NKOK-1005)/1-51(1985)	
Author(s) Finn Radner	Sponsoring organization	
Title and subtitle THE PROS AND CONS OF POSSIBLE ELECTRON TRANSFER STEPS IN AROMATIC NITRATION REACTIONS		
Abstract The possible involvement of <u>electron transfer</u> (ET) steps in <u>electrophilic aromatic nitration</u> (EAN) and <u>nitrous acid catalyzed</u> (NAC) nitration has been examined. From calculations based on the <u>Marcus theory</u>, the <u>nitronium ion</u> was predicted to undergo non-bonded ET only from extremely <u>easily oxidizable aromatics</u>. The <u>nitrosonium ion</u> was predicted to be an effective ET oxidant for easily oxidizable aromatics, in agreement with experimental findings. Some less easily oxidizable aromatics that are susceptible to NAC nitration were predicted and found not to be oxidized by the nitrosonium ion. The <u>coupling reactions</u> of aromatic radical cations with <u>nitrogen dioxide</u>, a key step in the ET mechanisms of EAN and NAC nitration, have been demonstrated to yield products distinctive from those obtained by either nitration method. Hence, the possibility of an ET step in EAN, as well as in NAC nitration, was ruled out. The formation of radical cations under conditions of EAN has been suggested to result either from oxidation by nitrosonium ion impurities or via <u>homolytic dissociation of the σ-complex</u>. The formation of radical pairs on the reaction path of NAC nitration has been proposed to result via initial attack by a novel electrophile, <u>nitrosated dinitrogen tetroxide</u>, and subsequent dissociation of the initially formed σ-complex. The <u>nitrating properties</u> of <u>dinitrogen tetroxide</u> toward <u>polycyclic aromatic hydrocarbons</u> (PAH) have been examined. Nitro-PAH:s were formed in excellent yields via the mechanism suggested for NAC nitration. <u>Some comments on free radical nitration</u> involving nitrogen dioxide have been made.		
Classification system and/or index terms (if any)		
Supplementary bibliographical information		Language
ISSN and key title		ISBN
Recipient's notes	Number of pages	Price
	Security classification	

Distribution by (name and address) Organic Chemistry 3, Chemical Center, University of Lund, P.O. Box 124, S-221 00 Lund, Sweden

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Signature Finn Radner

Date September 6, 1985

Hanging on in quiet desperation
is the English way
The time is gone the song is over,
thought I'd something more to say

R. Waters

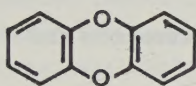
This review is a summary of results from the following papers, which will be referred to by the Roman numerals I-VII.

- I. L. Eberson, L. Jönsson and F. Radner
Nitration of aromatics via electron transfer; the relevancy of experiments involving generation of naphthalene radical cation in the presence of nitrogen dioxide.
Acta Chem. Scand. B 32 (1978) 749-753.
- II. L. Eberson and F. Radner
Nitration of aromatics via electron transfer. II. On the reaction between naphthalene radical cation and nitrogen dioxide.
Acta Chem. Scand. B 34 (1980) 739-745.
- III. F. Radner
Nitration of polycyclic aromatic hydrocarbons with dinitrogen tetroxide. A simple and selective synthesis of mononitro derivatives.
Acta Chem. Scand. B 37 (1983) 65-67.
- IV. L. Eberson and F. Radner
Electron transfer reactions in organic chemistry. VI. Possible role of electron transfer in aromatic nitration by nitrosonium and nitronium ion.
Acta Chem. Scand. B 38 (1984) 861-870.
- V. L. Eberson and F. Radner
Nitration of polycyclic aromatic hydrocarbons by dinitrogen tetroxide. II. Synthetic and mechanistic aspects.
Acta Chem. Scand. B 39 (1985) 343-356.
- VI. L. Eberson and F. Radner
Nitration of aromatics via electron transfer. IV. On the reaction between perylene radical cation and nitrogen dioxide or nitrite ion.
Acta Chem. Scand. B 39 (1985) 357-374.
- VII. L. Eberson and F. Radner
Nitration of reactive aromatics via electron transfer. V.

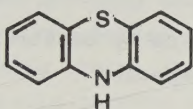
On the reaction between nitrogen dioxide and the radical cation hexafluorophosphates of some methyl-substituted naphthalenes.

Acta Chem. Scand. B 40 (1986). In press.

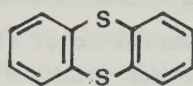
Structural formulae of compounds discussed:



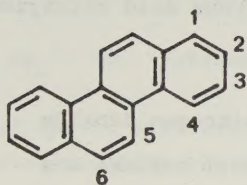
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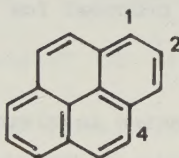
Phenothiazine



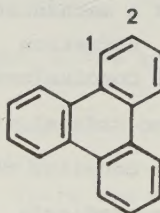
Thianthrene



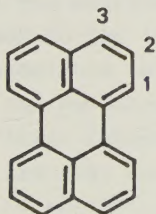
Chrysene



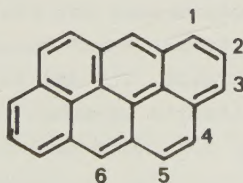
Pyrene



Triphenylene



Perylene



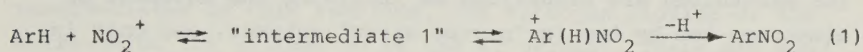
Anthanthrene

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1. INTRODUCTION

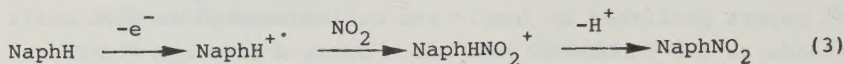
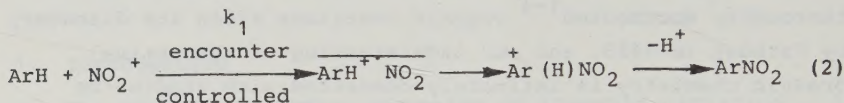
Nitration has remained one of the most studied and thoroughly documented¹⁻⁴ organic reactions since its discovery by Faraday in 1825, and our understanding of theoretical organic chemistry is intimately connected with studies on electrophilic aromatic nitration (EAN).^{1a} The impressive series of papers published by Ingold and collaborators² in 1950 still stands as the fundament from which today's research frontiers extend. However, the limitations involved with the use of the nitronium ion as the model electrophile and nitration as a model reaction for electrophilic substitution and for studies of aromatic reactivity are becoming increasingly obvious with increasing knowledge about the series of events frequently associated with EAN.^{1b} Among these, attack at ipso-positions, lack of substrate selectivity between sufficiently reactive aromatics, pronounced medium effects and interference from nitrous acid catalyzed (NAC) nitration, together with a continuing debate³ on the nature of the pre-association step to form the "first intermediate"⁴ or "encounter pair"^{1c} of eqn (1),



all add up to a situation in which, citing Schofield, "speculation about the mechanisms of nitration, is far from complete, nor is it ever likely to be. There are certainly surprises to come".^{1b}

Although not emerging as a "surprise", since the original ideas date back to the 1940's,^{5,6} one such speculation has received considerable interest since its presentation in 1977. By proposing the encounter-controlled formation of a radical pair as the "first intermediate" of eqn (1), Perrin⁷ claimed the electron transfer mechanism of aromatic nitration [eqn (2)] to be capable of providing better explanations for ipso-reactivity, positional reactivity and substrate selectivity than eqn (1). Experimental evidence was sought in the similarity of the α/β ratio in the formation of nitronaphthalenes by EAN and via reaction of nitrogen dioxide with anodically generated naphtha-

lene radical cation [eqn (3)].



The work leading to this thesis was to a large extent initiated by ideas from the Perrin paper. Four major themes can be discerned in the papers summarized in this review, and all of these are intimately related to the reactions in eqns (2) and (3). The four themes to be discussed in the following are the electron transfer and the radical coupling steps of eqn (2), the nitrating properties of dinitrogen tetroxide, and the mechanism of nitrous acid catalyzed nitration.

The electron transfer step. Traditionally, organic reaction mechanisms are visualized as involving the movement of electrons two by two in "curved arrow" schemes, and only in later years have suggestions of organic electron transfer reactions become abundant.⁸ Although the hypothesis that electron transfer should be a common feature of most aromatic substitution reactions has been shown to be invalid,⁹ great theoretical interest nonetheless remains for the case of aromatic nitration. A study on the ET oxidizing properties of the nitronium ion was therefore undertaken, the results of which are summarized in Section 2.3.

The radical coupling step. The coupling reaction of an aromatic radical cation with nitrogen dioxide has been suggested in many reaction schemes of recent years.^{7,10-24} Thus, in addition to EAN,¹⁰⁻¹² nitrous acid catalyzed nitration,¹⁸⁻²⁰ nitramine rearrangements²¹⁻²³ and electrophilic *ipso*-substitutions^{14,24} have all been suggested to involve such a step. However, knowledge of the nature and outcome of the reaction between a properly identified radical cation and a radical is very limited.²⁵ A number of radical cation salts was therefore

synthesized and subsequently treated with nitrogen dioxide. The results are summarized in Section 2.2.

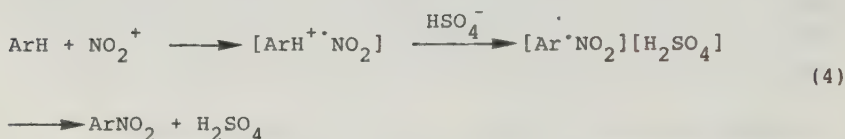
The nitrating properties of dinitrogen tetroxide. Nitrogen dioxide and its dimer, dinitrogen tetroxide, are nitrating agents.^{17,26-48} Since preparations of aromatic radical cations necessarily contain a certain amount of the parent compound, the possibility that nitroaromatics may be formed via dinitrogen tetroxide nitration, in addition the radical coupling reaction, had to be accounted for in the experiments mentioned above. A study was therefore undertaken on the reactions between dinitrogen tetroxide and a number of aromatic compounds. The results are summarized in Section 3.2.

The mechanism of nitrous acid catalyzed nitration. The catalytic effect of nitrous acid on aromatic nitration has traditionally been explained by the occurrence of a separate reaction, involving nitrosation followed by oxidation of the intermediate nitrosoaromatic compound.^{1d,49-52} As mentioned above, in recent years radical cations have been suggested as intermediates in this reaction, and nitrogen dioxide or the nitrosonium ion claimed to be the ET oxidant. There are many similarities between dinitrogen tetroxide nitration and nitrous acid catalyzed nitration, and the ET oxidizing properties of the nitrosonium ion (Section 2.3) and of nitrogen dioxide (Section 3.3) have therefore been examined. Based upon these results and on studies of the reactions between aromatic radical cations and nitrite ion, a mechanistic proposal for NAC and N_2O_4 nitration is presented (Section 3.4).

2. THE ELECTRON TRANSFER MECHANISM OF AROMATIC NITRATION

2.1 General aspects

In the mid-forties, Kenner⁵ and Weiss⁶ suggested that aromatic substitution reactions proceed via an initial electron transfer step, followed by proton loss and radical coupling [eqn (4)]. In the years to follow, the product-forming intermediate in nitration was identified as the σ -complex of eqn



(1), and hence the radical pair of eqn (4) had to be rejected.

The role of ET was next given theoretical support in the charge-transfer (CT) mechanisms presented by Nakagura and Tanaka⁵³ [eqn (5)] and by Brown.⁵⁴ Although both representations were based on Mulliken's concept of the resonance inter-



action between the no-bond and CT structure,^{55*} they differ in some important aspects,^{53c} most noticeably in the assumed structures of the intermediates involved.**

Pedersen and coworkers⁵⁶ provided further evidence in that the logarithmic plot of overall rate constants for substitution vs. ionization potentials was correctly predicted for the nitric acid/acetic anhydride nitration of a series of polycyclic aromatic hydrocarbons (PAH:s)⁵⁷ (see, however,

* $[\text{ArH}, \text{NO}_2^+] \longleftrightarrow [\text{ArH}^{+\cdot}, \text{NO}_2]$

** Brown postulates two unsymmetrical CT complexes as stable intermediates. For recent discussions on the CT interpretation, see Refs. 89 and 90.

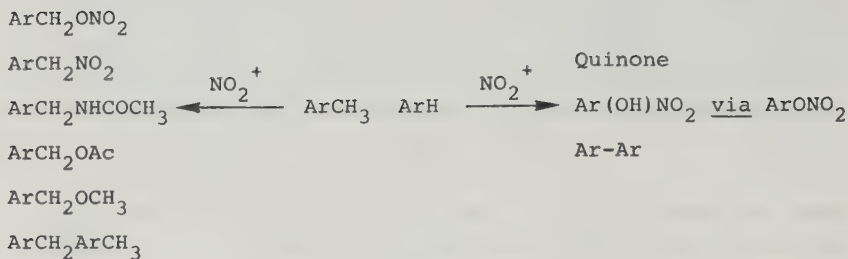
Section 3.5). Based upon the observed correlation between the orientation of substitution and the hyperfine coupling constants in the ESR spectra of the aromatic radical cations, it was suggested that substitution would occur at the position of the radical cation carrying the highest unpaired electron density.

Early experimental evidence favouring the ET mechanism of aromatic substitution includes the observation of ESR spectra of aromatic radical cations during the chlorination of hexamethylbenzene⁵⁸ and in substitution reactions of alkyl-substituted phenols.⁵⁹ However, it was not until the publication of the review by Todres⁹ and, especially, the previously mentioned paper by Perrin,⁷ that the mechanism received more general attention.

The Perrin modification of the ET mechanism [eqn (2)] was proposed in order to account for the paradox* of intramolecular, but not intermolecular, selectivity in the encounter-limited nitronium ion nitration of aromatics more reactive than toluene. Experimental evidence, in addition to the comparison of the results of the electrochemical nitration with those of EAN, was provided by the determination of the following anodic half-wave potentials in acetonitrile vs. Ag/0.01M Ag⁺: 1.82 (NO₂), 1.34 (naphthalene), 1.62 (mesitylene) and > 1.9 V (toluene). Based on these data, ET to NO₂⁺ was suggested to be exothermic for all aromatics more reactive than toluene. Positional selectivity was suggested to arise from the radical pair collapse owing to the non-uniform spin density of the radical cation. Ipso-reactivity in, e.g., the polyalkylbenzenes was, analogously, suggested to result from the high spin densities as the ipso-positions of the corresponding radical cations. Finally, nitro migrations were viewed as being mediated by radical pairs, as originally suggested by White.²¹

An additional benefit of the ET mechanism is, as pointed out in Paper I, that it is capable of providing simple explanations for many of the side-reactions encountered in aromatic nitration (Scheme 1), the electrochemical counterparts of which are known or supposed to be mediated by radical cations.⁶⁰

* For a discussion of this apparent paradox, see Ref. 1i.



Scheme 1

The characteristic features of the ET mechanism that can be subjected to experimental tests are the ET step and the radical cation - radical coupling step. These steps will be the subjects of the following two sections.

2.2 Reactions of aromatic radical cations with nitrogen dioxide

The controlled potential electrolysis of naphthalene in acetonitrile in the presence of nitrogen dioxide leads, according to Perrin,⁷ to the formation of nitronaphthalenes with approximately the same α/β ratio as that observed in EAN, as shown in Table 1. Repetition of the above experiment (Paper I) invariably resulted in the formation of nitronaphthalenes with a considerably higher α/β ratio than that observed in nitration by NO_2BF_4 . Moreover, the yield of nitronaphthalenes was dependent on temperature in the electrolysis experiment, which is improbable behaviour for a radical coupling step of low or zero activation energy. Since the higher α/β ratio was also obtained when naphthalene was treated with N_2O_4 in dry acetonitrile in the presence of added acid (e.g., methanesulfonic acid, MSA), it could be established that the "electrochemical" nitration above was in fact nitration by dinitrogen tetroxide, catalyzed by anodically generated acid. The current was consumed in oxidizing naphthalene to form dehydrooligomers and -polymers, and a small yield of binaphthyl and nitrobinaphthyl could be detected. Similar results, and support for this interpretation, have subsequently been presented by Achord and

Table 1. Isomer distributions for the nitration of naphthalene in acetonitrile with different reagents at 25 °C.^a

Conditions for nitration	Isomer ratio, α/β	Ref.
"Electrochemical"	9	7
HNO ₃ , H ₂ SO ₄ , urea	11	7
"Electrochemical"	20	Paper I
NO ₂ BF ₄ , CH ₃ CN	11	Paper I
N ₂ O ₄ , MSA, CH ₃ CN	23	Paper I

^a For a discussion of naphthalene nitration and a list of α/β ratios, see Ref. 91.

A different approach was therefore utilized (Paper II). The anodic oxidation of naphthalene (NaphH) at low current density and temperature in dichloromethane/tetrabutylammonium hexafluorophosphate (TBAPF₆) causes electrocrystallization of [NaphH]₂PF₆, as originally reported by Fritz et al.⁶² This reasonably stable radical cation salt can be handled at low temperatures (< -30 °C) under dry nitrogen. From a series of repeated syntheses of the salt in both divided and undivided cells, and subsequent treatment of a suspension of the salt with (cold) NO₂ in dry dichloromethane, it could be established that

- a) virtually no reaction took place at -50 °C;
- b) bringing up the temperature to ca. -25 °C caused a reaction in which nitronaphthalenes were formed in good material and current yield;
- c) the resulting α/β ratio, ca. 40, was considerably higher than that observed from nitration by NO₂BF₄, ca. 15 at -30 °C, and
- d) control experiments clarified that nitration by N₂O₄ constituted only a minor source of nitronaphthalenes: the

value of α/β originating from radical coupling alone is of the order of 50-60.

These results necessitated the conclusion that the coupling reaction of naphthalene radical cation with nitrogen dioxide cannot be an elementary step of the electrophilic nitration of naphthalene. Unfortunately, no evaluation of the rate of the coupling reaction was possible; however, several observations pointed toward its being slower than diffusion controlled, probably considerably so.

In Paper VII the same approach was extended to some methyl-substituted naphthalenes and the same general observations were made. Thus, for all substrates the radical cation radical coupling reaction yielded nitro derivatives with isomer distributions different from those obtained in EAN, as well as in dinitrogen tetroxide nitration, as shown in Table 2.

Table 2. Ratio of most abundant α -nitro isomer (in EAN) to all other nitro isomers formed in the nitration of naphthalene and some methylnaphthalenes.

Substrate	NO_2^+	N_2O_4	$\text{ArH}^{+\cdot} + \text{NO}_2$
Naphthalene	11	25	> 40
1-Methylnaphthalene	1.3	1.9	7.3
2-Methylnaphthalene	1.3	1.9	7.0
1,4-Dimethylnaphthalene	5.8	1.7	0.05
1,8-Dimethylnaphthalene	2.3	7.3	> 12
2,3-Dimethylnaphthalene	3.3	3.3	9
2,6-Dimethylnaphthalene	3.5	5.3	9

However, whereas the less stable naphthalene radical cations did couple well with nitrogen dioxide, the more stable ones of perylene (PeH) (Paper VI) and pyrene (PyH) (Paper VII) failed. Treatment of radical cation salts of perylene, pre-

pared either by electrocrystallization,⁶³ $[(\text{PeH})_2\text{PF}_6]$, or by oxidation by iodine⁶⁴ in the presence of silver trifluoromethanesulfonate $[(\text{PeH})_{1.33}\text{CF}_3\text{SO}_3]$, with NO_2 under a variety of conditions did not lead to the clean formation of nitroperylene, and similar results were observed for $(\text{PyH})_2\text{PF}_6$. The obvious conclusion to draw from these findings is the following: although the radical cations of more difficultly oxidizable aromatics do couple with nitrogen dioxide, the coupling reaction cannot be an elementary step in the nitronium ion nitration of these substances. Not even the more easily oxidizable aromatics, e.g., perylene, regardless of whether or not NO_2^+ is capable of oxidizing them to their radical cations, can be suspected to be nitrated via the ET mechanism of eqn (2), since their radical cations do not couple with NO_2 . The discussion of the implications of these conclusions will be returned to below. First, however, a short summary of some other work on the radical coupling reaction will be given.

The radical cation of 1,4-dimethoxybenzene, anodically generated in micellar solution, couples with NO_2 to form 2-nitro-1,4-dimethoxybenzene.¹⁰ Under the reaction conditions the rate of nitration by N_2O_4 was negligible. In the gas phase at 10 torr several radical cations, e.g., those of benzene, toluene, mesitylene and, albeit very slowly, naphthalene, were found to yield the σ -bonded $\text{Ar}^+(\text{H})\text{NO}_2$ complex upon treatment with NO_2 . This reaction was claimed to be the "first example of a reaction of an aromatic radical cation with NO_2 to yield a nitroaromatic product".¹¹ Morkovnik, Okhlobystin and co-workers have presented the following evidence in favour of the ET mechanism:^{12a-e}

- a) the reactions $\text{ArH} + \text{NO}_2^+$ and $\text{ArH}^{+\cdot} + \text{NO}_2$ yield identical products for ArH = phenothiazine and dibenzo-p-dioxin;
- b) upon treatment of phenothiazine, naphthalene or dibenzo-p-dioxin with nitric acid in 80 % acetic acid, acetonitrile or trifluoroacetic acid, or with NO_2BF_4 in trifluoroacetic acid, the corresponding radical cations were detected by UV and/or ESR spectra.

In a later paper, Morkovnik^{12f} attributed these findings to oxidation by the nitrosonium ion, as have many other observations of radical cations under conditions of aromatic nitration. Finally, the coupling reaction has been suggested as a key step in the nitration of phenols by clay-supported ferric nitrate¹³ and in ipso-substitution reactions of 3-substituted indoles.^{14a,b}

2.3 Properties of the nitronium and nitrosonium ions as electron transfer oxidants.

2.3.1 Introduction

It was recently reported that no CIDNP effects could be observed in the nitronium ion mediated nitration of mesitylene.^{20a,*} Since the observation of such an effect necessitates the existence of a radical pair along the reaction path, the (reverse) result suggests that mesitylene is not oxidized to its radical cation by NO_2^+ . As noted above, the observations of UV or ESR spectra of radical cations under conditions of aromatic nitration can in many cases be attributed to oxidation by the nitrosonium ion. While the experimental evidence for the action of NO_2^+ as an ET oxidant is limited,⁶⁵ NO^+ is a well established ET oxidant.^{12f,66-68} For example, NOBF_4 was successfully used to prepare the radical cation tetrafluoroborates of a series of easily oxidizable aromatics/heteroaromatics.⁶⁶ Since NO^+ ($E^\circ = 1.51 \text{ V}$) and NO_2^+ ($E^\circ = 1.56 \text{ V vs. NHE}$)** have almost identical E° values,^{69a} a detailed study on their ET oxidizing properties appeared desirable.*** In Paper IV the feasibility of non-bonded ET from aromatic compounds to the two ions was assessed in terms of the Marcus theory. In the following section a short summary of this treatment is

* Further remarks on or criticism of the ET mechanism can be found in, for example, Refs. 15 and 92.

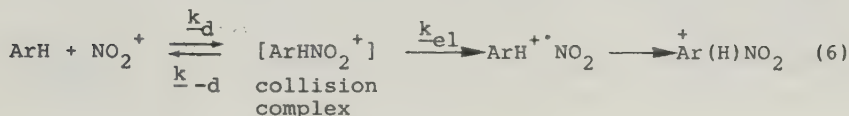
** All E° values given are referred to this standard.

*** Preliminary accounts of this work are given in Refs. 8 and 93.

presented, principally aiming at exemplifying the usefulness of the theory as a sorting device for suspected ET reactions.

2.3.2 The Marcus treatment

As mentioned earlier, nitronium ion nitration of aromatics more reactive than toluene proceeds at a diffusion controlled rate, i.e., with a rate constant of the order of $10^{10} \text{ M}^{-1} \text{ s}^{-1}$. If the ET mechanism, given in a slightly modified version in eqn (6), is to be operating, the overall rate and hence the rate of formation of the radical pair [k_1 of eqn (2)] must



reach this limit. Therefore from calculated values of k_1 it is possible to tell that:

- a) when $k_1 \approx 10^{10} \text{ M}^{-1} \text{ s}^{-1}$, ET might take place and further testing appears relevant;
- b) when $k_1 \ll 10^{10} \text{ M}^{-1} \text{ s}^{-1}$, the possibility of ET is ruled out and another mechanism must be operating.

In order to obtain values of k_1 for a series of relevant ArH:s the Marcus theory for non-bonded ET was applied.⁸ Knowing the standard free energy change for ET (ΔG^0), the reorganization energy needed to reach the transition state for ET (λ), the value of the collision number (Z) and the rate constants for formation and dissociation of the collision complex (k_d , k_{-d}), values of k_1 can be calculated from eqn (7). The λ -values for the reactions of ArH with NO_2^+ and NO^+ were calculated to be 75 and 40 kcal/mol, respectively, and in Table 3 some values of k_1 of special interest are presented.

$$k_1 = \frac{k_d}{1 + \frac{k_{-d}}{Z} \exp \left[\frac{\lambda}{4} \left(1 + \frac{\Delta G^0}{\lambda} \right)^2 / \frac{RT}{\right]} \quad (7)$$

Table 3. Calculated $\log k(M^{-1}s^{-1})$ for ET between ArH and $NO_2^+(NO^+)$ in acetonitrile at 25 °C.

Compound (E^O/V)	$\Delta G^O(NO_2^+)/$ kcal mol ⁻¹	$\log k(NO_2^+)$	$\log k(NO^+)$
Benzene(3.03)	34	-16.4	-13.3
Toluene(2.61)	24	-11.5	- 7.1
Mesitylene(2.43)	21	- 9.5	- 4.7
Naphthalene(2.08)	12	- 5.9	- 0.4
Pyrene(1.60)	1	- 1.7	4.3
Perylene(1.30)	-6	0.9	6.8
Ferrocene(0.60)	-22	5.7	10.2
(0.17)		10.0	10.3

Obviously NO^+ is by far the most effective oxidant. NO_2^+ exhibits, on the average, a 10^{-5} times slower rate of ET to a common substrate. This difference can be attributed to the large reorganization energy needed to reach the transition state for ET, in which considerable bending of the linear nitronium ion must occur. No such effect is present with NO^+ . To conclude, while the nitrosonium ion can be predicted to be an effective non-bonded ET oxidant, the nitronium ion should undergo non-bonding ET only from extremely easily oxidizable substrates only (with $E^O < 0.2$ V vs. NHE).

2.3.3 The nitrosonium ion - a powerful ET oxidant

In order to qualitatively assess the oxidizing behaviour of NO^+ toward substrates in the borderline region between "oxidizable" and "non-oxidizable", the work of Bandlish and Shine⁶⁶ on the oxidation of aromatics and heteroaromatics with $NOBF_4$ in acetonitrile or dichloromethane [eqn (8)] was extended



to a series of PAH:s. The results for some substrates of particular interest are summarized in Table 4. It should be noted that this method represents a very convenient way of preparing radical cation salts, since the other reaction product, nitric oxide, escapes the reaction mixture as a gas. On the compounds capable of undergoing ET to NO^+ with a high degree of conversion, pyrene and dibenzo-p-dioxin have the highest E° values. Therefore an E° value of ca. 1.6 V represents the upper limit for oxidation by the nitrosonium ion. The calculated k_1 value for pyrene (Table 3), $2 \times 10^4 \text{ M}^{-1}\text{s}^{-1}$, is in reasonable agreement with these qualitative findings. Note, however, that both reaction products of eqn (8) are capable of "escaping", and hence drive the equilibrium to the right;

Table 4. Properties of NO^+ as a one-electron transfer oxidant toward aromatic and heteroaromatic compounds.

Substrate	E° or $E_1/2/\text{V}^a$	Result ^b
Ferrocene ^c	0.60	RC formed in solution
Phenothiazine ^d	0.71	RC salt isolated
9,10-Dimethylantracene ^c	1.11	RC formed in solution
Perylene ^{c,d}	1.30	RC formed in solution and as solid
Thianthrene ^d	1.52	RC formed in solution
Pyrene ^c	1.60	RC formed in solution ^e
Dibenzo-p-dioxin ^d	1.63	RC formed in solution
Chrysene ^c	1.88	< 1 % RC formed at equilibrium ^e
Naphthalene ^c	2.08	No reaction
Triphenylene ^c	2.12	No reaction

^a From Ref. 69b, vs. NHE. ^b RC = radical cation. ^c Paper IV.

^d Ref. 66. ^e The RC solution was not stable upon standing.

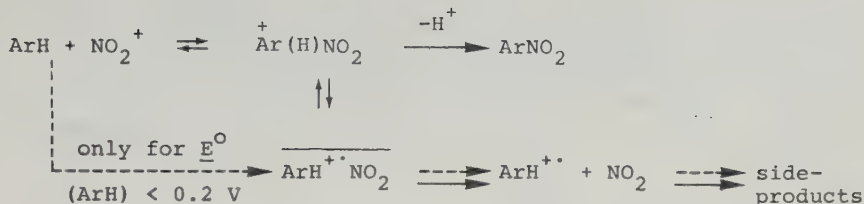
nitric oxide by virtue of being a gas, and the radical cation, most noticeably for those in the borderline region, via reaction with the solvent or nucleophiles adventitiously present.

On the other hand, aromatics with E° values higher than 2.0 V should not be oxidized by NO^+ , as inferred from both calculated and experimental results, despite the observation of CIDNP effects in the NAC nitration of, e.g., mesitylene.^{20a} This question will be returned to in Sections 3.1.3 and 3.4.

2.3.4 What about the nitronium ion, then?

The results of the Marcus treatment rule out the possibility of the nitronium ion acting as an ET oxidant in virtually all practical cases of aromatic nitration. However, it is not sufficient to attribute all observations of radical cations, and definitely not all the side-reactions observed in aromatic nitration, to the action of NO^+ . Moreover, ferrocene cannot be nitrated by NO_2^+ . Instead ferricinium ion is formed,⁶⁵ and later destroyed, under the reaction conditions. This behaviour is followed by other very reactive aromatics. However, here nitroaromatics can be formed via other routes, making the overall reaction schemes fairly complex. In Paper V this is exemplified with perylene as the archetype of an easily oxidizable arene.

In Section 2.2 the reluctance of the perylene radical to couple with NO_2 was pointed out. Treatment of perylene with nitric acid in strongly acidic media results in the formation of a tarry reaction product, containing only low yields of mononitroperylene. (Mononitration of perylene is preferentially carried out with N_2O_4 /dichloromethane, as discussed in Section 3.2). In order to account for these observations, a reaction scheme involving polar association/homolytic dissociation (Scheme 2) was proposed. The thermodynamics of this pathway are governed by exactly the same factors as that of ET. Hence, from the ΔG° values included in Table 3 it can be estimated that for a substrate with an E° value lower than ca. 1.55 V this pathway will be exergonic. This provides a simple explanation for the impossibility of nitrating ferrocene with



Scheme 2

NO_2^+ : the equilibrium $\text{FcH} + \text{NO}_2^+ \rightleftharpoons \text{FcH}^{+\cdot} + \text{NO}_2$ lies so far to the radical pair side that not even the addition of a base (e.g., 2,6-di-*t*-butyl-4-methylpyridine) will drive the reaction toward the formation of FcNO_2 . For a sufficiently reactive aromatic compound, homolytic dissociation of the Wheland intermediate will compete with deprotonation, and since the radical cation/nitrogen dioxide formed not will couple once escaped from the initial cage, the formation of by-products via further reactions of the radical cation will increase with increasing acidity of the nitrating system. In order to conceptualize the difference between ET and polar attack, we note that in order to reach the transition state for ET all bending of the linear nitronium ion has to be accounted for energetically, whereas for direct bond formation the bond energy gain from the incipient C-N bond partially compensates for the O-N-O bending energy expended.

Additionally we can now understand why the naphthalene, but not the perylene radical cation couples with nitrogen dioxide. Using the previously given values of $\underline{E}^{\text{O}}$, the reaction $\text{ArH} + \text{NO}_2^+ \rightleftharpoons \text{ArH}^{+\cdot} + \text{NO}_2$ is found to be exergonic (0.26 eV) in the perylene case and endergonic (0.52 eV) in the naphthalene case. As shown in Fig. 1 the σ -complex is necessarily higher in energy than the ArH/NO_2^+ couple (by Δ_{PeH} and Δ_{NpH} , respectively). Therefore, formation of the σ -complex must be endergonic [$(\Delta_{\text{PeH}} + 0.26)$ eV] in the perylene case and exergonic [$(\Delta_{\text{NpH}} - 0.52)$ eV] in the naphthalene case (assuming $\Delta_{\text{NpH}} \approx 0.1 \text{ eV}^{1\text{e}}$).

Finally, we may note that the homolytic dissociation step of Scheme 2 has been suggested previously, although in a some-

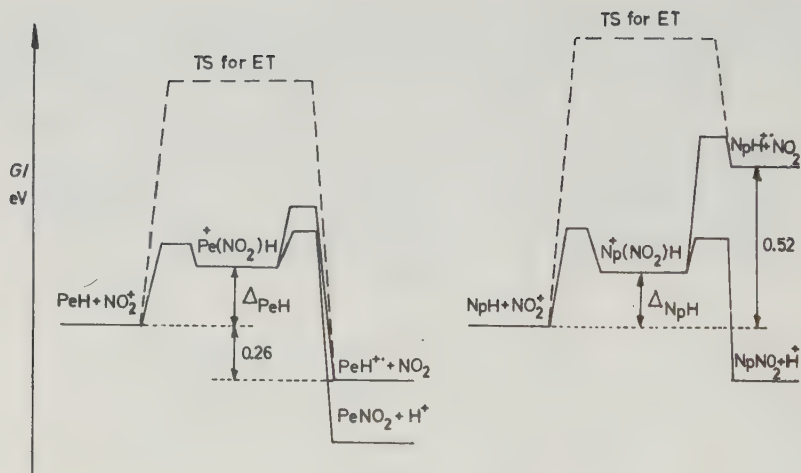
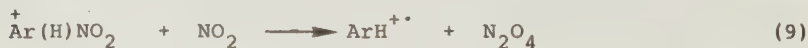


Fig. 1. Schematic free energy diagrams for the reaction $\text{ArH} + \text{NO}_2^+ \longrightarrow \text{ArH}^{++} + \text{NO}_2$ for (a) perylene and (b) naphthalene.

what different version. In order to explain the retarding effect of N_2O_4 on nitration by N_2O_5 , Gold suggested the following reaction to be operating [eqn (9)].⁷⁰



2.4 Conclusions

As pointed out more than once in this section, the ET mechanism of eqn (2) must be considered invalid. This is due to
 a) the low ET oxidizing power of the nitronium ion, and
 b) the clear non-involvement of the radical cation radical coupling step in EAN as inferred from the distinctive isomer ratios observed in the radical coupling reactions of the less stable radical cations and from the refusal of the more stable ones to couple

with NO₂.

The evidence presented earlier in favour of the ET mechanism can be explained either by oxidation by nitrosonium ion impurities⁷¹ or by the polar association/homolytic dissociation mechanism of Scheme 2.

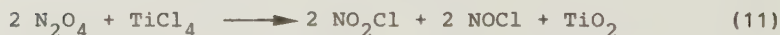
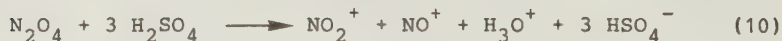
3. NITRATION OF AROMATICS BY DINITROGEN TETROXIDE AND OTHER N(III)/N(IV) SPECIES

3.1 Introduction

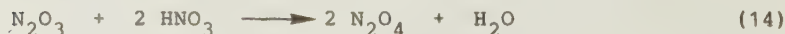
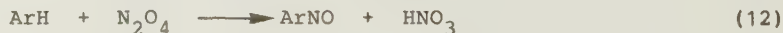
In the preceding sections the nitrating properties of dinitrogen tetroxide and the catalytic effect of nitrous acid upon aromatic nitration have been mentioned repeatedly. In recent years, the mechanism(s) involved has been the subject of much debate, most notably concerning the possible involvement of an electron transfer step. However, before embarking on this discussion, a summing up of some other work is necessary (Sections 3.1.1-3.1.2).

3.1.1 Nitration by dinitrogen tetroxide

In sulfuric acid solution or in the presence of Lewis acids, the nitrating properties of N_2O_4 are normally explained by nitronium ion nitration, as shown in eqns (10) and (11).^{1f,43a} Similar explanations were given for the N_2O_4



nitration of toluene and anisole in trifluoroacetic acid in the presence of urea.⁴⁷ However, in the nitration of 1,4-dimethoxybenzene in carbon tetrachloride,³⁹ and of some polyalkylbenzenes in nitromethane,⁴⁰ involvement of the nitronium ion could be ruled out, and instead nitration via nitrosation (Scheme 3, see Section 3.1.3 below) was suggested to be operating.



Scheme 3

Upon treatment with N_2O_4 or nitrous vapours in organic solvents reactive aromatics such as acenaphthene,³⁶ acenaphthylene,³⁷ anthracene,^{28-32a} fluorene,³⁶ naphthalene,^{26-28,32c} phenanthrene,^{28,32a-35} N,N-dimethylaniline^{38b,42} and some methoxybenzenes^{38a,41} have all been demonstrated to yield nitrated products. The formation of by-products in some of these reactions has been attributed to either addition of NO_2 - NO_2 across formal double bonds³¹ or initial radical attack^{32-34,37} (see Section 4).

Interesting to note in this context is the formation of nitrated PAH:s upon the exposure of the parent PAH to environmental sources of nitrogen (and sulfur) oxides. These reactions are of general environmental importance, as inferred from the presence of PAH:s and nitrogen oxides in exhaust gases from the combustion of fossil fuels, as well as from the well-documented mutagenic properties of nitro-PAH:s.⁴⁵⁻⁴⁸ In a study on the nitration of a series of PAH:s under environmentally relevant conditions, the reaction was demonstrated to be of an electrophilic nature and the possible involvement of electron transfer from the PAH to NO_2 or NO^+ was noted.^{48a}

3.1.2 Nitrous acid catalyzed nitration

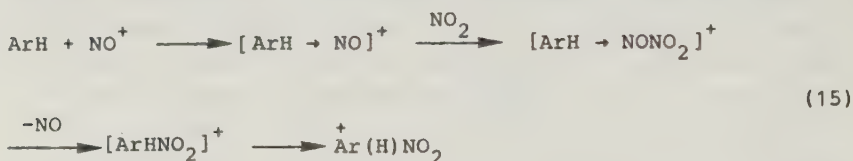
Nitrous acid plays a dual role in connection with aromatic nitration. On the one hand, it exerts a pronounced anti-catalytic effect on nitrations of up to moderately reactive aromatics, caused either by reducing the steady-state concentration of nitronium ion or by deprotonating the nitric acidium ion ($H_2NO_3^+$).^{1g} On the other hand, a similarly pronounced catalytic effect is observed in the presence of nitrous acid in the nitration of a number of more reactive aromatics, as first observed for aniline and phenol.^{1g} Based on numerous observations, such as

- a) the change of the o/p ratio from 2.7 in the uncatalyzed to 0.1 in the nitrous acid catalyzed nitration of phenol;^{49b}
- b) the resemblance of the latter o/p ratio to that from the nitrosation of phenol;⁵⁰
- c) the isolation of some p-nitrosophenol from the nitra-

tion of phenol;^{49a}

a mechanism involving nitration via nitrosation was proposed [Scheme 3;³⁹ originally HNO_3 was considered the oxidant of eqn (13)].⁴⁹ Other substrates that have been found or suggested to be subjected to nitration via nitrosation include anisole, *p*-nitrophenol,^{49b,52} mesitylene,^{49b} 1-methylnaphthalene⁵¹ and anthanthrene.⁵¹

Another mechanistic proposal for NAC nitration for the specific cases of pentamethylbenzene and (possibly) durene involves the initial formation of a π -complex between the aromatic compound and NO^+ [eqn (15)].⁷² A similar interpretation

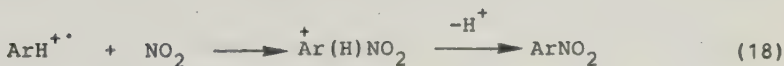
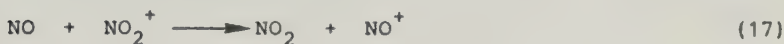
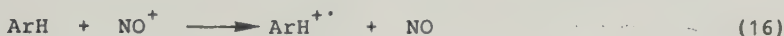


was made by Milligan for the nitration of benzene and toluene by N(III) and N(IV) species in trifluoroacetic acid. Intermediate nitrosation was found not to be involved, as evidenced from the only partial formation of nitrobenzene from nitrosobenzene and N_2O_4 .⁴⁴

3.1.3 Role of electron transfer in NAC nitration

Catalysis of nitration by nitrous acid (or generally N(III)/N(IV) species) has been observed for a number of reactive substrates under conditions where nitration via nitrosation could not be held responsible. Ross et al. observed that the catalysis or promotion by N(III) species of the nitration of phenol resulted in an *o/p* ratio of 0.78, inconsistent with the value of 0.03 observed for nitrosation.^{73a} Both naphthalene^{73b} and 1,2,3-trimethoxynaphthalene¹⁹ were nitrated by mixtures of nitric and nitrous acids under conditions where either acid alone was found to be ineffective. Explanations for this behaviour were sought or discussed in relation to the findings by Giffeny and Ridd^{18a} on the reac-

tion between N,N-dimethylaniline (Me_2NArH) and nitric acid. They interpreted the formation of p-nitro-N,N-dimethylaniline and N,N,N',N'-tetramethylbenzidine as initial oxidation by NO^+ to form a radical pair, $\text{Me}_2\text{NArH}^+\cdot\text{NO}$, followed by either oxidation, radical coupling and deprotonation as in Scheme 4 to yield the nitro compound, or dissociation of the radical pair and subsequent dimerization of the radical cations to yield the benzidine. The intermediacy of a radical pair on the reaction pathway leading to the p-nitro product was later established by the observation of CIDNP effects,^{18b} and



Scheme 4

similar observations have been made using mesitylene,^{20a} p-nitrophenol^{20b} and durene^{20c} as substrates. Eqn (17) was found not to be responsible for the oxidation of NO since the overall rate of NAC nitration greatly exceeded that of NO_2^+ formation.^{20a}

In the following sections the general features and synthetic utility of dinitrogen tetroxide nitration (3.2) and the ET oxidizing properties of nitrogen dioxide (3.3) will be presented in order to provide a firm basis for a continued discussion on the role of ET in NAC nitration in Section 3.4.

3.2 General features of dinitrogen tetroxide nitration

As mentioned previously nitration by N_2O_4 can constitute a major source of nitroaromatics in the type of experiments on the radical coupling reaction discussed in Section 2.2. The observation of the very clean and rapid formation of nitroperylene from perylene and N_2O_4 in dichloromethane initiated a study (Paper III) on the general synthetic utility of the

reaction. In Table 5 two characteristic features of the reaction are illustrated. (1) For the less reactive aromatics a catalytic amount of a strong acid must be added in order for the reaction to proceed at a convenient rate, i.e. > 98 % conversion in 3 h. (2) The reaction exhibits greater selectivity than the hitherto preferred reagent for the nitration of PAH:s, nitric acid in acetic anhydride.^{57,74,75}

Table 5. Nitration of polycyclic aromatic hydrocarbons.

PAH	Acid catalyst added? ^a	Isomer distribution ^b	
		N ₂ O ₄ /CH ₂ Cl ₂ ^c	HNO ₃ /Ac ₂ O ^d
Perylene	No	3-/1- > 100	3-/1- = 23
Pyrene	No	Solely 1-	Solely 1-
Anthracene	No	Solely 9- ^e	Solely 9-
Chrysene	Yes	6-/others = 32	6-/others = 9
Naphthalene	Yes	1-/2- = 34	1-/2- = 11
Triphenylene	Yes	2-/1- = 3.1	2-/1- = 1

^a See text. ^b E.g., 6-/others = ratio of the 6-nitro isomer to all other nitro isomers formed. ^c Paper III. ^d Paper III in agreement with Refs. 57a (pyrene, triphenylene), 57b (naphthalene, perylene), and 57c (chrysene). ^e Ca. 5 % anthraquinone was also formed.

Moreover, whereas nitration by HNO₃ in acetic anhydride is associated with tedious work-up procedures and possible by-product formation with more reactive substrates, nitration by N₂O₄ proceeds without by-product formation (except for a few substrates, as discussed in Section 4), and with a very simple overall experimental set-up. It can therefore be regarded the best synthetic method yet found for the synthesis of small amounts of nitro-PAH:s. Note that when purities in the 99.9 % range are required, e.g., for mutagenic studies, the final

purification should be performed by HPLC, as described by Greibrook et al.⁷⁵

The beneficial effect of added acid on the reaction was demonstrated in Paper II to be related to the strength of the acid. Thus, trifluoroacetic acid was found to be almost ineffective at concentration levels at which methanesulfonic acid caused significant catalysis of the nitration of naphthalene. In Paper V this effect was subjected to a quantitative study. Table 6 summarizes the effects of added acids and bases on the nitration of chrysene [0.01 M] in dichloromethane at 20 °C, with $[N_2O_4] = 0.075$ M, i.e. the stoichiometric concentration according to eqn (22) below.

Table 6. Nitration of chrysene by dinitrogen tetroxide.

Additive (concentration/M)	Yield of nitro-chrysenes/%	Reaction period /min
None	3	3
CH ₃ COOH (0.002)	4	3
CF ₃ COOH (0.002)	12	3
p-CH ₃ C ₆ H ₄ SO ₃ H (0.002)	94	3
CH ₃ SO ₃ H (0.002)	96	3
CF ₃ SO ₃ H (0.002)	100	3
NOBF ₄ (0.0005)	97	3
None	37	40
2,6-di-t-C ₄ H ₉ -4-CH ₃ -pyridine (0.01)	0.1	40
(C ₄ H ₉) ₄ NNO ₂ (0.001)	9	40

While the reaction rates for all substrates examined were sensitive to additives of the types included in Table 6, the isomer distributions remained unaffected with the exception of that for perylene (see Section 4). In the absence of additives, the rate of nitration fairly nicely correlated with the ease of oxidation of the substrate (Fig. 2). The approximate second-order rate constants, k_2 , were obtained with

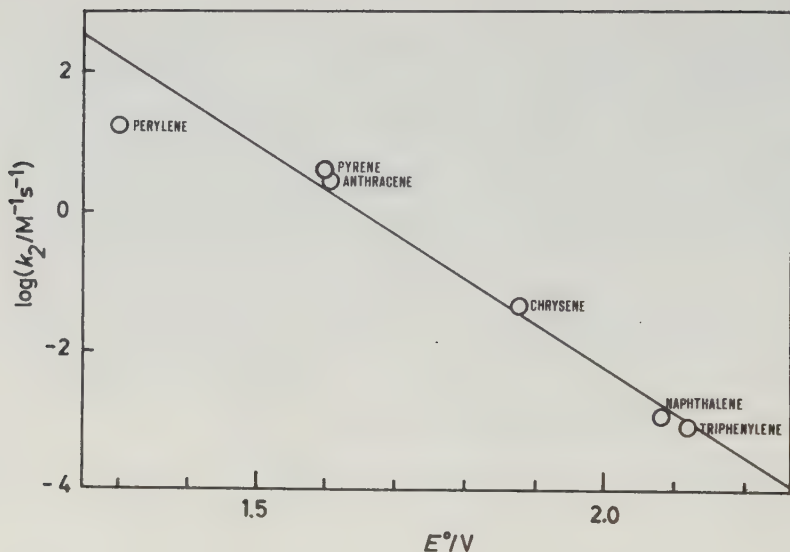
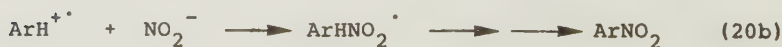
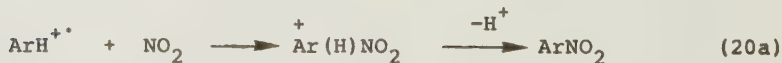
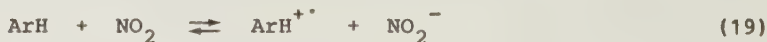


Fig. 2. Plot of $\log k_2$ vs. E° for the nitration of some PAH:s by nitrogen tetroxide in dichloromethane at 25 °C.

[ArH] = 0.01 M and $[N_2O_4] = 0.075$ M.

A similar set of data was simultaneously presented by Pryor and coworkers.¹⁷ Since the relative reactivities observed in their investigation were found to correlate better with the assumption of initial ET than electrophilic attack, the following mechanism was proposed (Scheme 5).



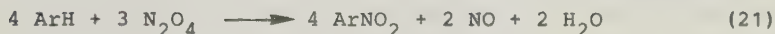
Scheme 5

Before focusing on the ET oxidizing properties of NO_2 ,

the following observations concerning the stoichiometry of the reaction should be noted (Paper V):

- a) As previously observed by Milligan,⁴⁴ NO is produced during the reaction. The amount collected in a rather crude series of experiments was 0.5 mol NO/mol N₂O₄, corresponding to 75 % of the amount theoretically required by eqn (21) below.
- b) The formation of water, 0.35 ± 0.05 mol H₂O/mol N₂O₄ (70 % by theory) could be detected by GLC.
- c) Conversion of 100 % ArH into ArNO₂ ensues when 0.75 mol N₂O₄/mol ArH has been added. Further addition has either no immediate effect, e.g., for chrysene, or lowers the yield, as in the case of perylene.*

These observations are summed up in the following equation [eqn (21)]:



3.3 Properties of nitrogen dioxide as ET oxidant

As shown above, and by Pryor et al., the rate of nitration fairly nicely correlated with $\underline{E}^{\circ}$, which can be considered a measure of the reactivity toward one-electron oxidation of the PAH. In order to evaluate whether or not nitrogen dioxide is an ET oxidant powerful enough toward PAH:s for an initial rate-determining ET step to be feasible, the Marcus treatment was applied to eqn (19) (Paper V).

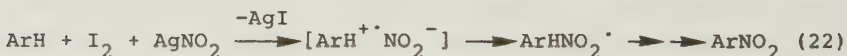
A somewhat different way of reasoning from the applied to NO⁺ and NO₂⁺ in Section 2.3.2 was utilized. Instead of estimating the range of substrate $\underline{E}^{\circ}$ values capable of yielding

* This observation was missed in Paper III. Dinitration is a fairly slow process, except for substrates as reactive as perylene, e.g., benz[a]pyrene.⁹⁴ Substrates less reactive than chrysene can be successfully mononitrated with excess N₂O₄ provided that the reaction periods are not prolonged.

the maximum value of k_1 for a given value of the reorganization energy, k_1 values were taken from the observed second-order rate constants for the reaction $\text{ArH} + \text{N}_2\text{O}_4$ (Paper V). From these rate constants and the corresponding substrate E° values, λ was calculated using a slightly modified version of eqn (7), i.e., eqn (70) of Ref. 8. Using $E^\circ(\text{NO}_2/\text{NO}_2^-) = 0.25 \text{ V}$, the estimated λ value of eqn (19) comes out at $28 \pm 30 \text{ kcal/mol}$. Obviously, the present data cannot at all be fitted to the Marcus equation. The expected reorganization energy, calculated from $\lambda = 0.5 \times [\lambda(\text{NO}_2/\text{NO}_2^-)] + [\lambda(\text{ArH}^{+\cdot}/\text{ArH})]$ is 40 kcal/mol , implying that the ET step of eqn (19) must be deemed improbable unless the above value of $E^\circ(\text{NO}_2/\text{NO}_2^-)$ is too low by 0.65 V .

In keeping with this result, the back ET reaction of eqn (19) was shown to be rapid and quantitative for $\text{ArH}^{+\cdot} = \text{naphthalene}^{+\cdot}$ (Paper II), perylene $^{+\cdot}$ (Paper VI), pyrene $^{+\cdot}$ and (2-methylnaphthalene) $^{+\cdot}$ (Paper VII). Since even the perylene radical cation is instantaneously reduced by nitrite ion, nitrogen dioxide apparently cannot act as an ET oxidant toward the majority of aromatic compounds.

These results also imply that the formation of nitro-PAH:s resulting upon treatment of the PAH with iodine and silver nitrite [eqn (22)] is not a radical cation mediated process



in the way suggested by Ristagno and Shine.⁷⁶ Since the reaction of iodine with silver nitrite in the absence of the PAH yields nitrogen dioxide and silver iodide,⁷⁷ and since the method can only be applied to PAH:s equally or more reactive than pyrene,⁷⁶ the formation of nitro-PAH:s obviously must be attributed to nitration by dinitrogen tetroxide (Paper V).

3.4 A mechanistic proposal for NAC nitration

Although treated separately in the preceding text, nitration by dinitrogen tetroxide and NAC nitration can be regarded as merely being variations on a common theme (Paper V). For instance, the α/β ratio observed from NAC nitration (23)^{73b}

and N_2O_4 nitration (24) of naphthalene are identical within the limits of error, and since nitrous acid in nitric acid to some extent exists as NO^+ , ^{1d,42,78} an equivalent of N_2O_4 ($\text{NO}^+ + \text{NO}_3^-$) is invariably present under NAC nitration conditions. We may therefore conclude that dinitrogen tetroxide in dichloromethane, with an acid catalyst added when necessary, constitutes a convenient system for mechanistic studies of NAC nitration.

At this stage, some remarks on the state of N_2O_4 in dichloromethane appear relevant. As summarized in Paper V, the literature clearly demonstrates the insignificance of dissociation into $\text{NO}_2^+/\text{NO}_2^-$. Instead, the following species can be present: N_2O_4 , NO_2 , NO^+ , NO_3^- and the ion pair NO^+NO_3^- . On addition of acids stronger than nitric acid, the formation of the ion pair will be increasingly favoured. The possible attacking species of the reaction can thence be found among the following alternatives:

- 1) NO_2 attacking as a free radical;
- 2) NO_2 attacking as an ET oxidant;
- 3) NO^+ attacking as an electrophile;
- 4) NO^+ attacking as an ET oxidant;
- 5) N_2O_4 , or a modification thereof, attacking as an electrophile.

The two pathways involving NO_2 can immediately be ruled out, since 1) the reaction exhibits much greater selectivity than expected for a free radical reaction, and 2) nitrogen dioxide is not a sufficiently powerful ET oxidant. At a first glance pathway 4) appears the most logical choice of the three remaining alternatives, as inferred from the observations of radical pairs on the reaction path of NAC nitration and from the correlation between rate of nitration and ease of oxidation of the substrate. There remains, however, a number of observations not immediately explicable by Scheme 4. Firstly, mesitylene undergoes NAC nitration via a pathway involving radical pairs, but according to the treatment in Section 2.3.2, NO^+ is not a sufficiently powerful ET oxidant to bring about this conversion. Moreover, naphthalene, with a lower E° value than mesitylene, is not oxidized by NOBF_4 in dichloromethane. The question then arises whether the oxidizing power of NO^+

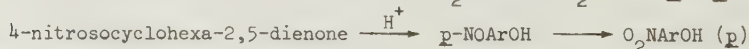
can be increased to the required extent in acidic media. Secondly, the almost complete absence of by-products in, e.g., the NAC nitration of naphthalene is not in good accordance with the intermediacy of such an unstable and reactive species as the naphthalene radical cation. Thirdly, the coupling reaction of the latter species with nitrogen dioxide yields nitronaphthalenes with an α/β ratio considerably higher than that observed in NAC nitration, whereas the radical cations of substrates capable of undergoing ET to NOBF_4 do not couple with nitrogen dioxide.

Therefore NO^+ , being a poor electrophile,^{*} reacts either via ET or, with less easily oxidizable aromatics, to form an $\text{ArH} \rightarrow \text{NO}^+$ π -complex,^{44,79} unless the aromatic is extremely susceptible to electrophilic attack, in which case nitrosation takes place (e.g., for $\text{ArH} = \text{phenol}^{**}$). Accordingly, the involvement of NO^+ as the attacking species in NAC nitration seems unlikely, and hence alternatives 3) and 4) can be ruled out.

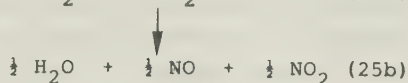
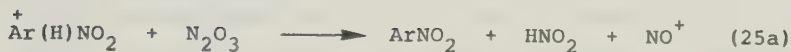
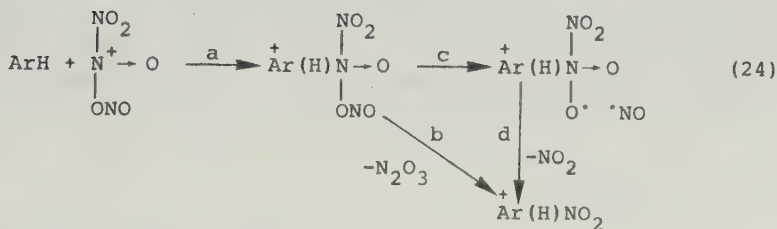
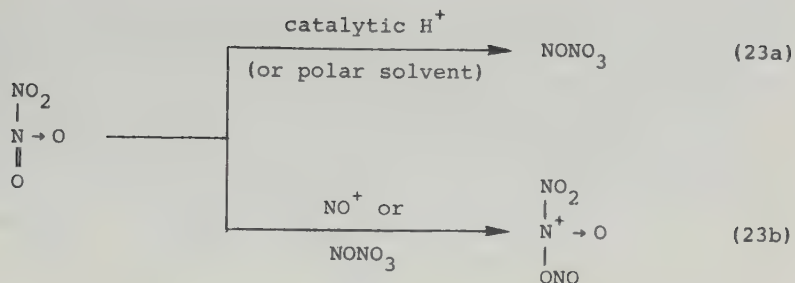
Left to be considered is then only alternative 5), electrophilic attack by some modified version of N_2O_4 . As concluded in Paper V nitrosated dinitrogen tetroxide, $\text{N}_2\text{O}_4\text{NO}^+$,^{***} appears to be the electrophile that provides the most reasonable set of explanations for the observations presented earlier. The formation and reactions of $\text{N}_2\text{O}_4\text{NO}^+$ are summarized in Scheme 6 below.

* The electrophilic reactivity of NO^+ has been estimated as 10^{-14} times lower than that of NO_2^+ .⁹⁵

** In a very recent study, Al-Obaidei and Moodie demonstrated that the reaction of phenol with $\text{HNO}_2/\text{HNO}_3$ in aqueous H_2SO_4 leads to the formation of *p*-nitrophenol via a nitrosation-oxidation scheme and of a 57:43 mixture of *o*- and *p*-nitrophenol via a NAC pathway. The following mechanism was proposed:⁹⁶



*** There are no reports concerning $\text{N}_2\text{O}_4\text{NO}^+$. NO_2NO^+ has been suggested to exist in $\text{N}_2\text{O}_4/\text{HNO}_3$,⁹⁷ and the bond-dissociation energy of $\text{NO}-\text{NO}^+$ has been determined to be 14 kcal mol⁻¹.⁹⁸



Scheme 6

An observation not mentioned in the preceding discussion is the considerable decrease in the rate of nitration of pyrene by N_2O_4 on changing the solvent from dichloromethane (93 % conversion in 10 min) to carbon tetrachloride (< 1 % conversion) (Paper V). Obviously, the formation of the ion pair [eqn (23a)] is almost completely inhibited in carbon tetrachloride, whereas in dichloromethane the equilibrium of eqn (23a) does not lie completely to the left, accounting for the possibility of nitrating perylene and pyrene without added catalyst. The catalytic effect of added acid or NO^+ is inherent in the scheme, whereas the addition of base retards the formation of NONO_3 . The high positional selectivity of the reaction relative to EAN can be at least partly attributed to the

bulkiness of $\text{N}_2\text{O}_4\text{NO}^+$ relative to NO_2^+ , explaining the preference for substitution at the less reactive but less hindered 2-position in triphenylene. It should also be noted that eqn (22) results when the equations of Scheme 6 are summed up.

The formation of a radical pair [eqn (24c)] without the involvement of direct electron transfer to NO^+ provides explanations for the observation of CIDNP effects as well as for the correlation of rate with oxidation potential, assuming that the stability of the unconventional radical cation $\text{Ar(H)NONO}_2\text{O}^+$ parallels that of the substrate radical cation. However, whether the formation of Ar(H)NO_2 from the first σ -complex of eqn (24) occurs via (24c) + (24d) or another pathway on which the required radical pair can be formed remains to be settled in future investigations.

3.5 Conclusions

Nitrogen oxide species are invariably present/autocatalytically formed in nitric acid, and preparations of nitronium salts are inherently contaminated with nitrosonium salts. Because of the rapid equilibria operating between NO species at different oxidation levels, the presence of NO^+ is unavoidable in many nitrating systems unless scavengers⁸⁰ are added. Although initial nitrosation is limited to the substrates that are extremely susceptible to electrophilic attack, the presence of NO^+ may nonetheless have a pronounced influence on the outcome of nitration reactions. If nitration by NO_2^+ is the reaction undergone by substrates of low or intermediate reactivity under a certain set of reaction conditions, increasing the reactivity of the substrate will enhance the possibility of interference due to reaction via the NAC pathway. For sufficiently reactive compounds, e.g., perylene, the presence of free NO_2^+ or NO^+ will eventually result in by-product formation due to side-reactions involving radical cations. These compounds are preferentially nitrated by N_2O_4 in dichloromethane without acid catalysis. Therefore, the relative reactivities reported by Dewar et al.⁵⁷ from the nitration of a series of reactive aromatics with fuming nitric acid in acetic anhydride are, as pointed out by Schofield,^{1h,51} not attribut-

able (at least not solely) to nitration by the nitronium ion. The previously mentioned (Section 2.1) correlation between these relative rates and the hyperfine coupling constants in the ESR spectra of the corresponding radical cation⁵⁶ must accordingly either be coincidental or somehow connected to nitration proceeding via the NAC pathway. Finally, it may be noted that the term "nitrous acid catalyzed nitration" is somewhat narrow and a better denomination would be, for example, "N(III)/N(IV) promoted nitration".

4. FREE RADICAL NITRATION INVOLVING NITROGEN DIOXIDE

The addition of a base or change to a less polar solvent has a pronounced retarding effect on the rate of nitration of e.g. pyrene by N_2O_4 in organic solvents. This effect can be attributed to inhibition of the formation of NONO_3 , as illustrated in Scheme 6. With perylene, however, a completely different behaviour emerges (Paper VI). Thus, while the rate of conversion of perylene was only slightly lowered, the ratio of the 3-/1- mononitro isomers decreased from ca. 100 in dichloromethane to ca. 2 in carbon tetrachloride or in dichloromethane containing a few mol % of a base. The most plausible explanation for these observations is a change in mechanism as less polar solvents are employed, as suggested from a plot of the $\log(3-/1- \text{ isomer ratio})$ vs. the polarity parameter, $^{81} E_T^N$, for a series of solvents (Fig. 3).

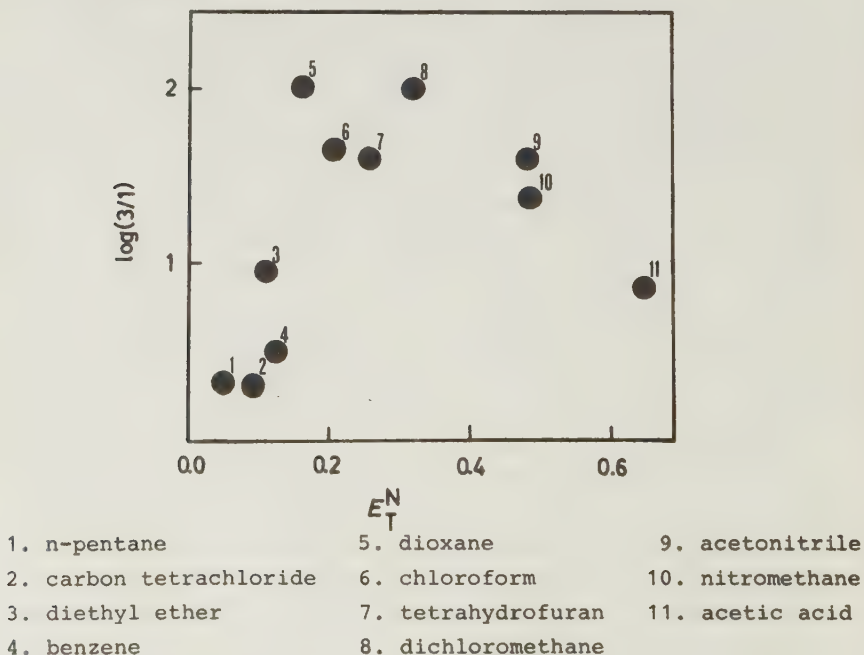


Fig. 3. Plot of $\log$ isomer ratio vs. the E_T^N solvent polarity parameter.

Radical processes are generally nonselective, and favoured in media of low polarity, and hence a pathway involving initial attack by NO_2 as a free radical [eqn (26)] was invoked in Paper VI to explain these findings. At least three pathways are possible for the further transformation of the nitroperylene radical:



- a) oxidation by NO_2 followed by proton loss from the σ -complex formed;
- b) addition of a second NO_2 and subsequent elimination of HNO_2 from the intermediate dinitrodihydro or nitro-nitritodihydroperylene;
- c) reaction with ArH and addition of a second NO_2 to yield a nitrotetrahydrobiperylene nitrate which decomposes to nitroperylene in the presence of a base in a way analogous to that observed in the case of phenanthrene.³⁴

Interesting to note here is the suggestion that the formation of a nitrocyclohexadienone from the reaction of a hindered phenol with NO_2 should be initiated by abstraction of the phenolic hydrogen to yield nitrous acid and a phenoxy radical.⁸²

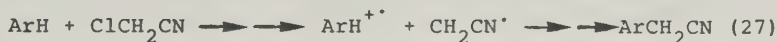
There are many examples of initial radical attack by NO_2 on olefins in the literature, and it is significant that the aromatic compounds demonstrated to be unsuitable for nitration by N_2O_4 in Paper V all contain bonds of more or less pronounced olefinic character, as in anthracene, phenanthrene and acenaphthylene. The formation of anthraquinone has been reported on a number of occasions, and most recently Pryor and coworkers explained its formation by trapping of the radical cation formed according to eqn (19) with water.¹⁷ Since anthracene cannot be oxidized by NO_2 , initial radical attack appears to provide a more reasonable explanation, but the lack of experimental data prevents reliable speculations on the further steps of the reaction.

On the other hand, the number of reports concerning free-radical nitration⁸³ of aromatics by NO_2 is very small. Olah and Overchuck found toluene to be nitrated by NO_2 in nearly

statistical o:m:p ratio at high temperature when subjected to irradiation by UV light,⁸⁴ and as a result of somewhat similar conditions 2-nitropyrene was detected in environmental samples,⁴⁸ NO_2^+ as well as N_2O_4 yielding solely 1-nitropyrene. Coombes et al. suggested that the very slow conversion of toluene into nitrotoluenes (o:m:p = 39:44:17) presumably was mediated by a species of radical nature.⁸⁵ Apparently much work remains to be done in this area in order to obtain a unifying picture of these processes.

5. THE COUPLING REACTION BETWEEN RADICAL CATIONS AND FREE RADICALS

During the course of this work, a literature search revealed an almost complete lack of knowledge about the coupling reaction of radical cations with radicals other than NO_2 . Oxidative substitution of ferrocene, e.g. cyanation, has been suggested to involve coupling of the ferricinium ion with the appropriate radical,^{86,87} and photochemical aromatic cyanomethylation has been proposed to proceed via the pathway outlined in eqn (27).²⁵ However, the isomer distributions presented (i.e. for toluene o:m:p = 33:47:20) fall much better in



line with a radical process of the type discussed in Section 4 (for toluene o:m:p = 37:38:25)⁸⁴ than with the very high regioselectivity observed for the $\text{ArH}^{+\cdot} + \text{NO}_2$ reaction discussed earlier. Therefore, reliable generalizations about radical cation radical coupling reactions cannot be made at present; it is, however, not unreasonable to presume that they are reactions that exhibit high regioselectivity. In Paper VII an attempt was made to correlate the reactivity toward NO_2 with the spin density for a given position in the radical cation,⁸⁸ since bond formation has been suggested to predominate at positions with high spin density.⁷ However, this correlation was only partly successful and, most notably, despite the much higher spin density at the 5- than the 2-position in the 1,4-dimethylnaphthalene radical cation, reaction with NO_2 yielded predominantly the 2-nitro isomer. Therefore, since the spin density is only one component determining the outcome of these reactions, further theoretical and experimental work will be needed for reliable rationalizations to be possible.

6. SUMMARY AND PERSPECTIVES

The possible involvement of an electron transfer step in electrophilic aromatic nitration has been subjected to theoretical and experimental testing. The nitronium ion is found to be incapable of oxidizing any aromatics of practical interest, and the presence of radical cations under conditions of aromatic nitration is suggested to result either from oxidation by nitrosonium ion impurities or via homolytic dissociation of the σ -complex $\text{Ar}(\text{H})\text{NO}_2^+$.

The question of an electron transfer step has also been probed for nitrous acid catalyzed nitration. Although the nitrosonium ion is capable of transferring an electron from more easily oxidizable aromatics, the reaction is suggested to not be mediated by electron transfer. Instead, replacing the traditional nitration via nitrosation interpretation, a mechanism involving attack by a novel electrophile, nitrosated dinitrogen tetroxide, is proposed.

The synthetic usefulness and possible mechanism of nitration by dinitrogen tetroxide in dichloromethane has been investigated. The method is found superior to other methods for the preparation of mononitrated polycyclic aromatic hydrocarbons, and the mechanism is suggested to be identical to that of nitrous acid catalyzed nitration, the two reactions only being variations on a common theme.

The nitration of perylene has been the subject of a detailed investigation. In media of low polarity, or in basic media, nitration by dinitrogen tetroxide does not operate and another mechanism, assumed to involve radical attack by nitrogen dioxide, is effective.

The suggestion that the only fragmentarily documented coupling reaction between a radical cation and a neutral radical should be favoured at the positions in the radical cation bearing the highest spin density has been tested. For the reactions of a series of methyl-substituted naphthalene radical cations with nitrogen dioxide only partial correlation is observed, in some cases overshadowed by a strong tendency toward the predominance of coupling in the ring bearing the

methyl substituent(s).

Finally, an outline of some possible future work related to this thesis seems to be appropriate:

a) It is postulated in Scheme 2 that homolytic dissociation of Ar(H)NO_2^+ competes with the normal deprotonation step during the nitronium ion nitration of very reactive aromatics. Provided that NO_2^+ can be obtained satisfactorily pure, and that NAC nitration can be completely inhibited, a study of the effects of added acids and bases on the NO_2BF_2 (or NO_2PF_6) nitration of very reactive PAH:s in, e.g., nitromethane, can be performed.

b) It is suggested in Paper II that the coupling reaction of ArH^{++} with NO_2 is not fast enough to be an elementary step of a reaction proceeding at an overall encounter-controlled rate. A kinetic study (stopped-flow) of the reaction between, for example, $(2\text{-CH}_3\text{-NaphH})_2\text{PF}_6$ and NO_2 , although technically difficult to perform, would be of interest, since virtually nothing is known about the rate of these reactions.

c) In Paper V, NO_2^+ is predicted to undergo non-bonded ET only from substrates with $\underline{E}^{\text{O}} < 0.2$ V. Although it appears very difficult to find a series of substrates with $0.0 < \underline{E}^{\text{O}} < 0.6$ V that are not susceptible to electrophilic attack by NO_2^+ , the prediction can in principle be checked using very pure NO_2^+ . Concerning the ET oxidizing properties of NO^+ , the question of the influence of acidic media (Section 3.4) on the oxidizing power remains to be answered. The determination of the rate of the reaction $\text{PAH} + \text{NO}^+ \longrightarrow \text{PAH}^{++} + \text{NO}$ would make possible a comparison with the rates calculated in Paper V.

d) The mechanism proposed for NAC nitration in Scheme 6 involves the action of $\text{N}_2\text{O}_4\text{NO}^+$ and the intermediacy of a radical pair. The former species can possibly be detected by ^{15}N NMR, while the radical pair can be sought for using ESR spectroscopy. Alternatively, CIDNP effects can be looked for in the reaction of N_2O_4 with a carefully chosen PAH.

e) In Section 4 perylene is suggested to be capable of being nitrated via a radical pathway. It would be of great interest to search for similar behaviour with other very

reactive PAH:s, and to establish whether or not anthracene to any extent reacts via an analogous pathway. The proposed¹⁷ trapping by water of the intermediate radical cation on the reaction path leading to the by-product anthraquinone can be checked by adding H_2^{18}O and analyzing for $[\text{M}^+ + 2]$ in the mass spectrum of the anthraquinone formed.

f) The limited knowledge about the outcome of reactions between a radical cation and a radical is pointed out in Section 5. It would be interesting to compare the reaction products from $\text{ArH}^{+\cdot} + \text{R}^{\cdot}$ with those of $\text{ArH} + \text{R}^+$ for R other than NO_2 . Unfortunately, most of the possible $\text{R}^{\cdot}$ (e.g., $\text{CN}^{\cdot}$, $\text{Br}^{\cdot}$) are more or less inaccessible under the required reaction conditions.

ACKNOWLEDGEMENTS

I would like to express my deep gratitude to Professor Lennart Eberson for his interest and guidance throughout this work.

In addition to numerous stimulating discussions, thanks are due to Dr. Lennart Jönsson for running the ESR spectra, Dr. Lars-Göran Wistrand for valuable comments on the manuscript, and Mr. Sven Ericson for interchange of results.

I also wish to acknowledge Dr. Robert E. Carter for linguistic criticism, Drs. Ulf Berg and Zoltan Blum and Mr. Rolf Servin for running the NMR spectra, Mr. Einar Nilsson for running the mass spectra, Messrs. Lars Trege and Ove Anderberg for valuable technical assistance, Mr. Martin Andrén for drawing some of the figures and Mrs. Heleen Hjalmarsson for her excellent typing of the manuscripts.

Finally, I would like to acknowledge the support and help given by my colleagues and friends.

Financial support by the Swedish Natural Science Research Council is gratefully acknowledged.

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